Atmospheric Chemistry of Perfluorinated Aldehyde Hydrates (n-$C_xF_{2x+1}CH(OH)_2$, $x = 1, 3, 4$): Hydration, Dehydration, and Kinetics and Mechanism of Cl Atom and OH Radical Initiated Oxidation

M. P. Sulbaek Andersen,[†] A. Toft,[‡] O. J. Nielsen,[†] M. D. Hurley,[§] T. J. Wallington,*,[§] H. Chishima,[||] K. Tonokura,[||] S. A. Mabury,[⊥] J. W. Martin,[⊥] and D. A. Ellis[⊥]

Department of Chemistry, University of Copenhagen, Universitet sparken 5, DK-2100 Copenhagen, Denmark, Department of Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark, Ford Motor Company, P. O. Box 2053, Dearborn, Michigan 48121-2053, Environmental Science Center, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, and Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

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Smog chamber/Fourier transform infrared (FTIR) techniques were used to measure $k(Cl+C_xF_{2x+1}CH(OH)_2)$ ($x = 1, 3, 4$) = $(5.84 \pm 0.92) \times 10^{-13}$ and $k(OH+C_xF_{2x+1}CH(OH)_2) = (1.22 \pm 0.26) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} in 700 Torr of N_2 or air at 296 ± 2 K. The Cl initiated oxidation of $CF_3CH(OH)_2$ in 700 Torr of air gave CF_3COOH in a molar yield of 101 ± 6%. IR spectra of $C_xF_{2x+1}CH(OH)_2$ ($x = 1, 3, 4$) were recorded and are presented. An upper limit of $k(CF_3CHO+H_2O) < 2 \times 10^{-23}$ cm^3 molecule^{-1} s^{-1} was established for the gas-phase hydration of CF_3CHO. Bubbling CF_3CHO/air mixtures through liquid water led to >80% conversion of CF_3CHO into the hydrate within the approximately 2 s taken for passage through the bubbler. These results suggest that OH radical initiated oxidation of $C_xF_{2x+1}CH(OH)_2$ hydrates could be a significant source of perfluorinated carboxylic acids in the environment.

1. Introduction

Long-chain perfluoroalkyl carboxylic acids (PFCAs, C_xF_{2x+1}-COOH, where $x = 6-12$) have been observed in fish[1,2] and mammals[3] in a range of locations around the world. PFCAs are not generally used directly in consumer or industrial materials, other than in aqueous film forming foams or as polymerization aids in fluoropolymer manufacture.[4] Thermolysis of fluoropolymers produces PFCAs;[5] however, the magnitude of this source appears insufficient to account for the observed global environmental burden of these compounds. While it cannot be ruled out that PFCAs may be transported long range via ocean currents,[6,7] an atmospheric transport route where polyfluorinated precursors are degraded to PFCAs is supported by recent atmospheric monitoring, atmospheric chemistry, and global atmospheric modeling studies.

Perfluorinated aldehydes, $C_xF_{2x+1}CHO$, are formed during the atmospheric oxidation of HFCs (hydrofluorocarbons), HCFCs (hydrochlorofluorocarbons), and fluorinated alcohols.[8,9] Atmospheric oxidation of perfluorinated aldehydes has been investigated[10−15] and offers a possible route to the formation of PFCAs. $C_xF_{2x+1}CHO$ form stable hydrates of the formula $C_xF_{2x+1}CH(OH)_2$. In fact, the aldehydes $C_xF_{2x+1}CHO$ ($x = 1-4$) are only available commercially in their hydrated forms. The stability of the hydrates is evident from the rigorous conditions required to liberate the aldehyde: distillation in the presence of phosphorus pentoxide.

$$C_xF_{2x+1}CHO + H_2O \Leftrightarrow C_xF_{2x+1}CH(OH)_2 \qquad (1)$$

Given the abundance of water (gas, liquid, and solid) in the environment and the relatively long lifetime (approximately 20 days[13]) of $C_xF_{2x+1}CHO$ with respect to reaction with OH radicals, it seems reasonable to speculate that hydration may be a significant atmospheric fate of $C_xF_{2x+1}CHO$. Unfortunately, there are no kinetic data available with which to assess the importance of hydration as an atmospheric loss mechanism for $C_xF_{2x+1}CHO$. Furthermore, there have been no studies of the atmospheric fate of $C_xF_{2x+1}CH(OH)_2$. At the present time it is difficult to make a quantitative assessment of the contribution of atmospheric oxidation of $C_xF_{2x+1}CH(OH)_2$ to the observed PFCA budget.

To improve this situation, we have used smog chamber Fourier transform infrared (FTIR) and NMR techniques to study the atmospheric chemistry of n-$C_xF_{2x+1}CH(OH)_2$ ($x = 1, 3, 4$). Studies of fluorinated alcohols[9] and acids[16] suggest that shorter chain length n-$C_xF_{2x+1}CH(OH)_2$ molecules will serve as useful models to understand the degradation mechanism of long-chain perfluorinated aldehyde hydrates. Straight-chain isomers were studied in the present work. For simplicity we will refer to these species as $C_3F_7CH(OH)_2$ and $C_4F_9CH(OH)_2$ in the rest of this article. The present study had four goals: first, to measure the reactivity of $C_xF_{2x+1}CH(OH)_2$ with respect to reaction with Cl atoms and OH radicals; second, to identify and quantify the products of the Cl atom and OH radical initiated oxidation of $C_xF_{2x+1}CH(OH)_2$; third, to establish the rate of hydration of $C_xF_{2x+1}CHO$ both in the gas phase and on contact with liquid water; finally, to investigate the rate of dehydration of $C_xF_{2x+1}CH(OH)_2$ in dry environments. Results are discussed with respect to the atmospheric chemistry and environmental impact of fluorinated organic compounds.

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* Corresponding author. E-mail: twalling@ford.com.
[†] University of Copenhagen.
[‡] University of Southern Denmark.
[§] Ford Motor Company.
[||] The University of Tokyo.
[⊥] University of Toronto.

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2. Experimental Section

Experiments were performed in a 140 L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[17] The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.

$$Cl_2 \xrightarrow{h\nu} 2Cl \tag{2}$$

OH radicals were generated by UV irradiation of CH_3ONO/NO/air mixtures.

$$CH_3ONO \xrightarrow{h\nu} CH_3O + NO \tag{3}$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \tag{4}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{5}$$

Reactant and product concentrations were monitored by in situ FTIR spectroscopy using an analytical path length of 27 m and a spectral resolution of 0.25 cm^{-1}. IR spectra were derived from 32 coadded interferograms (1.5 min data acquisition time). The steps in a typical experiment were (i) prepare reaction mixture in the chamber, (ii) acquire IR spectrum, (iii) irradiate mixture for 10−60 s, (iv) acquire IR spectrum, (v) compare IR spectra before and after UV irradiation, quantify reactant loss and product formation, and (vi) evacuate and flush chamber ready for next experiment. Calibrated reference spectra were acquired by expanding known volumes of reference materials into the chamber.

The relative rate method is a well-established and widely used procedure for measuring the reactivity of Cl atoms and OH radicals with organic compounds. Kinetic data are derived by monitoring loss of the reactant compound, $C_xF_{2x+1}CH(OH)_2$, relative to one or more reference compounds. The decays of the reactant and reference are then plotted using the expression

$$\ln\left(\frac{[\text{reactant}]_{t_0}}{[\text{reactant}]_t}\right) = \frac{k_{\text{reactant}}}{k_{\text{reference}}} \ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right) \tag{i}$$

where $[\text{reactant}]_{t_0}$, $[\text{reactant}]_t$, $[\text{reference}]_{t_0}$, and $[\text{reference}]_t$ are the concentrations of reactant and reference at times t_0 and t and k_{reactant} and $k_{\text{reference}}$ are the rate constants for reactions of Cl atoms or OH radicals with the reactant and reference.

Reactant and reference compounds were monitored using absorption features at the following frequencies (cm^{-1}): $CF_3CH(OH)_2$, 700−860 and 1000−1200; $C_3F_7CH(OH)_2$, 890−1000; $C_4F_9CH(OH)_2$, 700−900; CF_3COOH, C_3F_7COOH, and C_4F_9COOH, 1800−1850; CH_3Cl, 1400−1550; C_2H_2, 650−800; C_2H_4, 850−1050; CH_4, 1240−1380. Reference spectra of CF_3CHO, C_2F_5CHO, C_3F_7CHO, and C_4F_9CHO were taken from previous work in our laboratory.[13] Analysis of the IR spectra was achieved through a process of spectral stripping, in which small fractions of the reference spectrum were subtracted incrementally from the sample spectrum. The process is illustrated in the Supporting Information.

Experiments were performed at 296 ± 3 K in 700 Torr of air diluent. All reagents except CH_3ONO and $C_xF_{2x+1}CH(OH)_2$ were obtained from commercial sources at purities >99%. CH_3ONO was prepared by dropwise addition of concentrated H_2SO_4 to a saturated solution of $NaNO_2$ in methanol and was devoid of any detectable impurities using FTIR analysis. Samples of $C_xF_{2x+1}CH(OH)_2$ contained significant amounts of $C_xF_{2x+1}CHO$. Using repeated freeze−pump−thaw cycling, it was possible to remove all but a trace of $C_xF_{2x+1}CHO$ before use. Ultrahigh purity nitrogen and synthetic air diluent gases were used as received. All other commercial samples were used without further purification.

In smog chamber studies it is important to control for unwanted loss of reactants and products via dark chemistry, photolysis, and heterogeneous reactions. Control experiments were performed in which mixtures of $C_xF_{2x+1}CH(OH)_2$ and air diluent were left for 10−1000 min in the dark. A slow loss of $C_xF_{2x+1}CH(OH)_2$ was observed accompanied by the appearance of the corresponding aldehyde and H_2O. The loss followed first-order kinetics. It seems likely that heterogeneous dehydration on the chamber walls is responsible for this $C_xF_{2x+1}CH(OH)_2$ loss. Steps were taken to minimize the duration of the experiments. Individual experiments were conducted within approximately 10 min. Pseudo-first-order loss rates for dehydration were calculated from the control experiments (0.0016 min^{-1} for $CF_3CH(OH)_2$) and used to apply minor corrections (<2%) for $C_xF_{2x+1}CH(OH)_2$ loss via dehydration. Unless stated otherwise, quoted uncertainties are two standard deviations from least squares regressions.

All ^1H NMR spectra were obtained at 25 °C on a Varian Unity 500, three-channel spectrometer operating at the appropriate frequency. Samples were prepared by the addition of 500 μL of water to the aldehyde (CF_3CF_2CHO) in the NMR tube followed by the addition of 50 μL of D_2O to provide a lock signal. Spectra were referenced to the signal produced from HDO.

3. Results

3.1. Relative Rate Study of Cl + $C_xF_{2x+1}CH(OH)_2$ (x = 1, 3, 4) in 700 Torr of Air/N_2. The kinetics of reaction 6 were measured relative to reactions 7 and 8:

$$Cl + C_xF_{2x+1}CH(OH)_2 \rightarrow \text{products} \tag{6}$$

$$Cl + CH_4 \rightarrow \text{products} \tag{7}$$

$$Cl + CH_3Cl \rightarrow \text{products} \tag{8}$$

Initial concentrations were 1.65−7.64 mTorr of $C_xF_{2x+1}CH(OH)_2$, 79.3−438 mTorr of Cl_2, and either 7.49−15.9 mTorr of CH_4 or 28.5−31.3 mTorr of CH_3Cl in 700 Torr of air diluent. The observed loss of $C_xF_{2x+1}CH(OH)_2$ versus those of the reference compounds in the presence of Cl atoms is shown in Figure 1. As indicated in the previous sections a small (<2%) correction has been applied to the $C_xF_{2x+1}CH(OH)_2$ data to account for loss via dehydration. Linear least squares analysis of the data in Figure 1 gives $k_6/k_7 = 5.53 \pm 0.59$ and $k_6/k_8 = 1.28 \pm 0.13$. Using $k_7 = 1.0 \times 10^{-13}$ and $k_8 = 4.8 \times 10^{-13}$,[18] we derive $k_6 = (5.53 \pm 0.59) \times 10^{-13}$ and $(6.14 \pm 0.62) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The results from the two independent studies were in agreement within the combined experimental uncertainties. We choose to cite a final value for k_6, which is the average of the two determinations with error limits that encompass the extremes of the individual determinations. Hence, $k_6 = (5.84 \pm 0.92) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

As seen from Figure 1, there was no discernible effect of the chain length (x = 1, 3, 4) on the reactivity of Cl atoms toward $C_xF_{2x+1}CH(OH)_2$. This seems reasonable based upon expectations that the $C_xF_{2x+1}-$ group will not react with Cl atoms, and that its influence on the reactivity of the $-CH(OH)_2$ groups

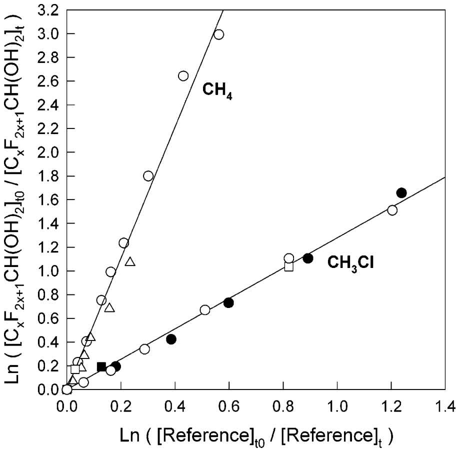

Figure 1. Decay of $CF_3CH(OH)_2$ (circles), $C_3F_7CH(OH)_2$ (triangles), and $C_4F_9CH(OH)_2$ (squares) versus CH_4 and CH_3Cl in the presence of Cl atoms in 700 Torr of air (solid symbols) or N_2 (open symbols) at 296 ± 2 K.

will not change markedly upon increasing x from 1 to 4. Hence, the results presented here can be generalized for all members of the family: $k(Cl+C_xF_{2x+1}CH(OH)_2) = (5.84 \pm 0.92) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.

This is the first study of the kinetics of gas-phase reactions involving $C_xF_{2x+1}CH(OH)_2$, and direct comparison with previous studies is not possible. Perfluorinated aldehyde hydrates are approximately a factor of 4 less reactive than their nonhydrated counterparts, $C_xF_{2x+1}CHO$, toward Cl atoms.[13] The observation that $C_xF_{2x+1}CH(OH)_2$ is less reactive than $C_xF_{2x+1}CHO$ is reasonable given the fact that both compounds react with Cl atoms via H-atom abstraction from the C−H bond and this bond is likely to be weaker, and hence more reactive, in the aldehyde than in the hydrate. The reactivity of $C_xF_{2x+1}CH(OH)_2$ toward Cl atoms is similar to that of $C_xF_{2x+1}CH_2OH$, $(6.48 \pm 0.53) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.[9] Abstraction of hydrogen from the O−H bond is thermodynamically unfavorable.[19] The fact that $C_xF_{2x+1}CH(OH)_2$ has a reactivity which is similar to that of $C_xF_{2x+1}CH_2OH$ indicates that the single C−H bond in $C_xF_{2x+1}CH(OH)_2$ is approximately twice as reactive as each of the two C−H bonds in $C_xF_{2x+1}CH_2OH$. The alcohol functionality is known to have an activating influence on C−H bonds, and hence the observed trends are in qualitative agreement with expectations.

3.2. IR Spectra of $CF_3CH(OH)_2$, $C_3F_7CH(OH)_2$, and $C_4F_9CH(OH)_2$. The IR spectra of $CF_3CH(OH)_2$, $C_3F_7CH(OH)_2$, and $C_4F_9CH(OH)_2$ were recorded in 700 Torr of air diluent at 296 K and are shown in Figure 2. The spectra were calibrated by monitoring the slow dehydration of $C_xF_{2x+1}CH(OH)_2$ within the chamber (see section 3.6), giving the corresponding aldehyde (and H_2O), quantifying the formation of the aldehyde,[20] and equating formation of aldehyde to loss of $C_xF_{2x+1}CH(OH)_2$. The integrated cross sections (650−1600 cm^{-1}) are $(1.97 \pm 0.20) \times 10^{-16}$, $(1.85 \pm 0.19) \times 10^{-16}$, and $(2.96 \pm 0.30) \times 10^{-16}$ cm^2 $molecule^{-1}$ for $CF_3CH(OH)_2$, $C_3F_7CH(OH)_2$, and $C_4F_9CH(OH)_2$, respectively. There are no previously reported IR spectra for these compounds.

3.3. Products of Cl Initiated Oxidation of $CF_3CH(OH)_2$ in 700 Torr of Air. The products of the Cl atom initiated oxidation of $CF_3CH(OH)_2$ were investigated by subjecting mixtures containing $CF_3CH(OH)_2$ and Cl_2 in 700 Torr of air diluent to UV irradiation. Figure 3 shows typical spectra acquired before (A) and after (B) a 21 s irradiation of a mixture of 7.04 mTorr of $CF_3CH(OH)_2$ and 83.7 mTorr of Cl_2, in 700 Torr of air diluent. The consumption of $CF_3CH(OH)_2$ was 23%.

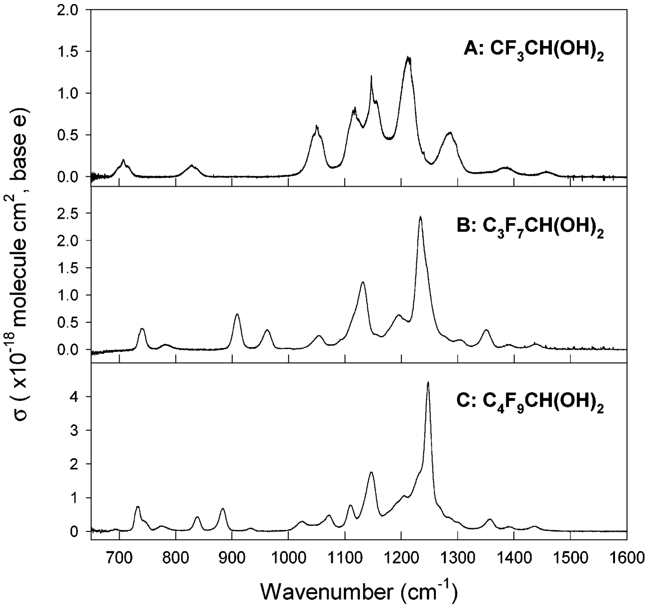

Figure 2. IR spectra of $CF_3CH(OH)_2$ (A), $C_3F_7CH(OH)_2$ (B), and $C_4F_9CH(OH)_2$ (C) recorded in 700 Torr of air at 296 ± 2 K.

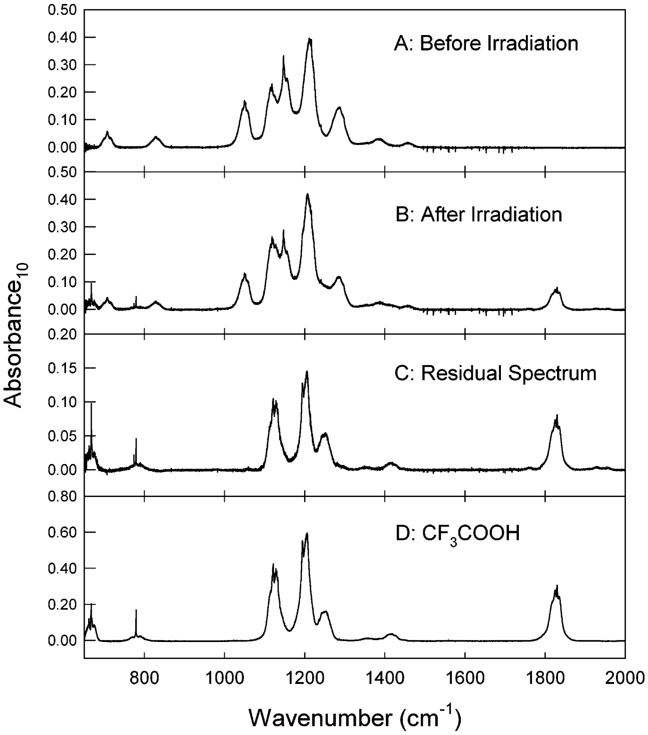

Figure 3. IR spectra obtained before (A) and after (B) a 21 s irradiation of a mixture of 7.04 mTorr of $CF_3CH(OH)_2$ and 83.7 mTorr of Cl_2 in 700 Torr of air. The consumption of $CF_3CH(OH)_2$ was 23%. Panel D is a reference spectrum of CF_3COOH.

Panel C shows the result of subtracting IR features attributable to $CF_3CH(OH)_2$ from panel B. Comparison of IR features in panel C with the reference spectrum shown in panel D reveals the formation of CF_3COOH in the system. No other carbon-containing product was detected.

Figure 4 shows a plot of the formation of CF_3COOH versus the loss of $CF_3CH(OH)_2$ observed for irradiations of mixtures consisting of 1.50−7.04 mTorr of $CF_3CH(OH)_2$ and 80.5−118 mTorr of Cl_2 in 700 Torr of air diluent. As seen from Figure 4, the concentration of CF_3COOH increased linearly with $CF_3CH(OH)_2$ loss, indicating that CF_3COOH is a primary product. The line through the data in Figure 4 is a linear least squares

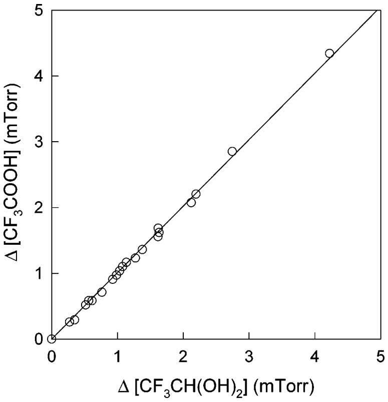

Figure 4. Yield of CF_3COOH from Cl atom initiated oxidation of $CF_3CH(OH)_2$ in 700 Torr of air.

fit (forced through zero) which gives a molar yield of 101 ± 6%. Quoted errors are two standard deviations from the regression analysis.

The simplest explanation for the observed product distribution is that reaction 9 is followed by reaction 10:

$$CF_3CH(OH)_2 + Cl \rightarrow CF_3C{\bullet}(OH)_2 + HCl \qquad (9)$$

$$CF_3C{\bullet}(OH)_2 + O_2 \rightarrow CF_3COOH + HO_2 \qquad (10)$$

By analogy to the reaction of CH_2OH radicals with O_2,[21] reaction 10 probably proceeds via the formation of a chemically excited peroxy radical, $[CF_3C(OO\bullet)(OH)_2]^*$, which decomposes rapidly to give the observed products.

It is of interest to compare the Cl atom initiated oxidation products of $CF_3CH(OH)_2$ with those of CF_3CHO. COF_2 is the major product of the Cl initiated oxidation of CF_3CHO in 700 Torr of air at 296 ± 2 K. There is little (in the absence of NO_x) or no (in the presence of NO_x) CF_3COOH formed in the oxidation of CF_3CHO.[11,13] In contrast, in the present study of the oxidation of $CF_3CH(OH)_2$ there was no detectable formation of COF_2, but CF_3COOH was observed in a yield indistinguishable from 100%. The gas-phase oxidation of the aldehyde and that of the hydrate give very different product distributions.

3.4. Relative Rate Study of OH + $CF_3CH(OH)_2$ in 700 Torr of Air.

The kinetics of reaction 11 were measured relative to reactions 12 and 13.

$$CF_3CH(OH)_2 + OH \rightarrow \text{products} \qquad (11)$$

$$C_2H_4 + OH \rightarrow \text{products} \qquad (12)$$

$$C_2H_2 + OH \rightarrow \text{products} \qquad (13)$$

Initial concentrations were 8.84−17.8 mTorr of $CF_3CH(OH)_2$, 88.6−110 mTorr of CH_3ONO, 0−15 mTorr of NO, and 2.82−6.02 mTorr of either C_2H_4 or C_2H_2 in 700 Torr of air diluent.

Photolysis of CH_3ONO is a convenient source of OH radicals for relative rate studies. However, CH_3ONO itself reacts with OH at a moderate rate ($k(OH+CH_3ONO) = 3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}[22]), scavenges OH radicals, and can make the loss of a less reactive compound difficult to measure. When working with compounds such as $CF_3CH(OH)_2$ that have modest reactivity toward OH radicals, an indirect variation of the relative rate technique (in which reactant loss is inferred from product formation) can be useful.[23] As discussed above, the oxidation of $CF_3CH(OH)_2$ gives CF_3COOH in essentially quantitative yield. CF_3COOH has characteristic IR features that are convenient to monitor. In the present work, the loss of $CF_3CH(OH)_2$ was inferred from the formation of its oxidation product CF_3COOH. By analogy to the results for Cl atom initiated oxidation presented in section 3.3, we assume that reaction of OH radicals with $CF_3CH(OH)_2$ gives CF_3COOH in 100% yield.

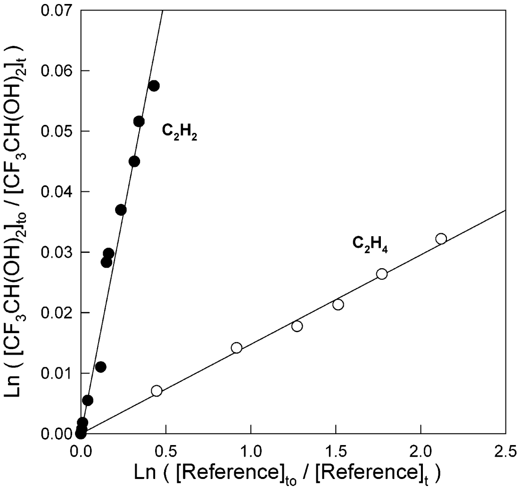

Figure 5. Decay of $CF_3CH(OH)_2$ versus C_2H_4 and C_2H_2 in the presence of OH radicals in 700 Torr of air at 296 ± 2 K.

Figure 5 shows the calculated loss of $CF_3CH(OH)_2$ versus the observed loss of the reference compounds, C_2H_2 and C_2H_4, when exposed to OH radicals in 700 Torr of air. Linear least squares fits to the lines through the data give $k_{11}/k_{12} = 0.0149 \pm 0.0014$ and $k_{11}/k_{13} = 0.146 \pm 0.015$. Using $k_{12} = 8.66 \times 10^{-12}$[24] and $k_{13} = 7.8 \times 10^{-13}$[25] gives $k_{11} = (1.29 \pm 0.12) \times 10^{-13}$ and $(1.14 \pm 0.12) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. It is gratifying to note the agreement between the experiments conducted with the two different reference compounds. We estimate that potential systematic errors associated with uncertainties in the reference rate constants and CF_3COOH yield could add an additional 10% to the uncertainty ranges for k_{11}. Propagating this additional uncertainty gives $k_{11} = (1.29 \pm 0.18) \times 10^{-13}$ and $(1.14 \pm 0.16) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. We choose to cite a final value for k_{11}, which is the average of those determined using two different reference compounds together with error limits that encompass the extremes of the individual determinations. Hence, $k_{11} = (1.22 \pm 0.26) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. As implied by the linearity of the plots in Figure 5, for the small consumptions of $CF_3CH(OH)_2$ used in the present study, loss of CF_3COOH via reaction with OH radicals will be of negligible importance[16] in the present work.

A methodology similar to that described above was pursued to determine the reactivity of OH radicals toward $C_xF_{2x+1}CH(OH)_2$, $x = 3$ and 4. Unfortunately, quantitative analysis of the acids C_3F_7COOH and C_4F_9COOH was not possible because of spectral interferences.

While there have been no previous studies of the reactivity of OH radicals toward $CF_3CH(OH)_2$, we can compare our results with previous studies of the reactivity of CF_3CHO. As discussed in section 3.1, the finding that perfluorinated aldehyde hydrates are less reactive than their perfluorinated aldehyde counterparts is confirmed with $CF_3CH(OH)_2$ being 5 times less reactive than CF_3CHO toward OH radicals.[13] Reaction of OH radicals with alcohols of the general formula $C_xF_{2x+1}CH_2OH$ proceeds with a rate constant of ≈1.0×10^{-13} cm^3 molecule^{-1} s^{-1} with no effect of fluorinated chain length.[9] The reactivity of OH radicals toward $CF_3CH(OH)_2$ is indistinguishable from that toward CF_3CH_2OH. As discussed in section 3.1, similar behavior was observed in the reactions with Cl atoms.

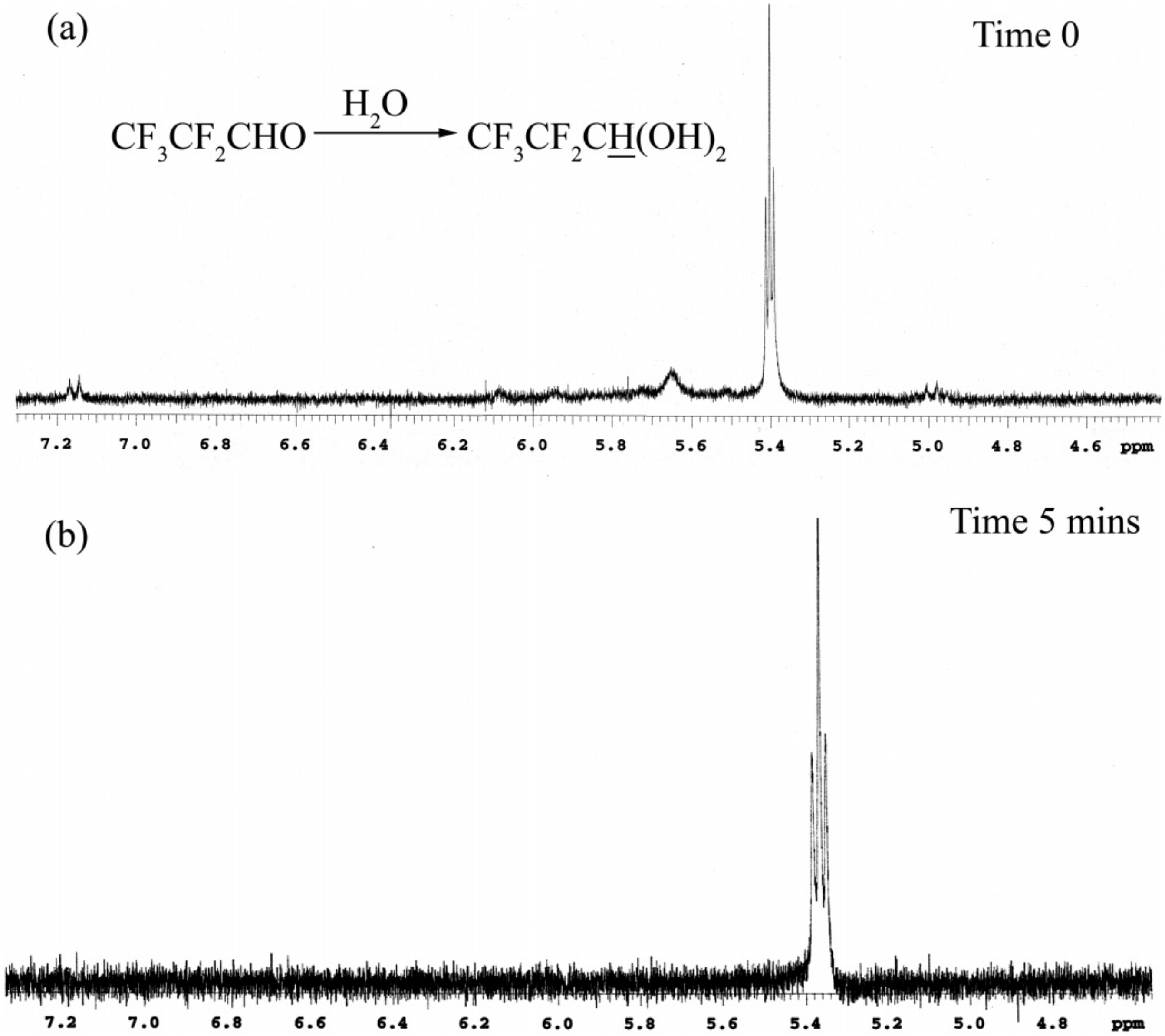

Figure 6. ^{1}H NMR observed upon the addition of water to the aldehyde C_2F_5CHO. The production of the corresponding hydrate is shown (a). The ^{1}H NMR recorded 5 min after the initial addition (b) indicates a loss of the hydrate produced from solution.

3.5. ^{1}H NMR Investigation of the Formation of $C_2F_5CH(OH)_2$ from C_2F_5CHO. To investigate the reaction of C_2F_5CHO with liquid water, a sample of approximately 0.1 mL of C_2F_5CHO was placed in an NMR tube and then 0.5 mL of water was added. The ^{1}H NMR was then recorded as soon as possible (within 3 min) upon addition of the water. Figure 6a shows the spectrum recorded. As can be seen from Figure 6a, the aldehyde is converted (within 3 min) to the hydrate, $CF_3CF_2CH(OH)_2$, which shows a characteristic triplet at 5.4 ppm. Figure 6b shows the ^{1}H NMR recorded 5 min after addition of water to the aldehyde. It can be seen from a comparison of the spectrum shown in Figure 6a that the signal-to-noise ratio has decreased significantly. It is suggested that this indicates the partition of the resultant hydrate into the headspace above the sample, perhaps indicating a significant water−air partition of the hydrate.

3.6. Hydration of CF_3CHO and Dehydration of $CF_3CH(OH)_2$ Studied in Smog Chamber. Three sets of experiments were conducted to study the hydration of CF_3CHO and the dehydration of $CF_3CH(OH)_2$ using the smog chamber. In the first set of experiments CF_3CHO/air gas mixtures were bubbled through liquid water to test for reaction of gas-phase CF_3CHO with liquid water. In the second set of experiments CF_3CHO/H_2O/air gas mixtures were prepared and left to stand in the dark in the smog chamber to test for reaction of gas-phase CF_3CHO with gas-phase water. In the third set of experiments $CF_3CH(OH)_2$/air mixtures were left to stand in the dark in a dry chamber to test for dehydration of $CF_3CH(OH)_2$.

In the first set of experiments a 5 L calibrated volume was filled with mixtures containing 0.53−1.30 Torr of CF_3CHO in 700 Torr of air. The smog chamber was then filled with 200−400 Torr of air, the contents of the 5 L calibrated volume were then swept through a glass frit bubbler and into the smog chamber using a stream of air until the total pressure in the chamber reached approximately 400−600 Torr, and air was then added to the chamber using the conventional gas handling system to reach a total pressure of 700 Torr. Gas flow through the bubbler lasted approximately 5 min. Three experiments were performed: The first experiment was conducted using a dry bubbler as a test for loss of CF_3CHO during passage through the experimental setup. There was no evidence for loss (<2%) of CF_3CHO, demonstrating our ability to introduce CF_3CHO

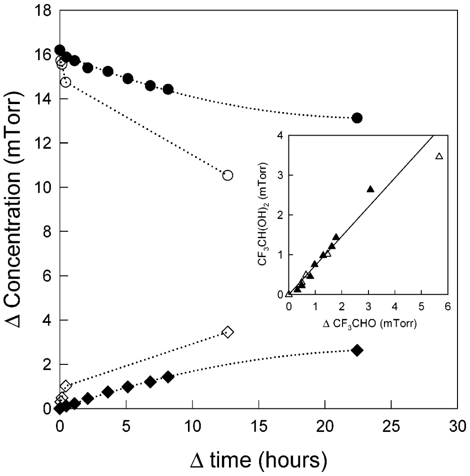

Figure 7. Decay of CF_3CHO (circles) and formation of $CF_3CH(OH)_2$ (diamonds) in two experiments where mixtures of 16.2 mTorr of CF_3CHO and 5 Torr of H_2O in 700 Torr of air were left in the dark for 13 h (open symbols) and 22 h (closed symbols). The insert shows a plot of the formation of $CF_3CH(OH)_2$ versus loss of CF_3CHO.

into the chamber using this method. In the second experiment the bubbler was filled with approximately 200 mL of deionized water (pH 7). The amount of CF_3CHO used in the 5 L volume was equivalent to a concentration of 20.1 mTorr in the 140 L chamber. After the CF_3CHO/air mixture was bubbled through the water and flowed into the chamber three compounds were identified; CF_3CHO, $CF_3CH(OH)_2$, and H_2O in concentrations of 2.8 mTorr, 0.8 mTorr and 5.9 Torr, respectively. Presumably the balance (82%) of the sample, remained as CF_3CHO and/or $CF_3CH(OH)_2$ in solution in the bubbler. The third experiment was conducted using water at pH 2 and with an amount of CF_3CHO in the 5 L volume corresponding to a concentration of 44.2 mTorr in the chamber. After the CF_3CHO/air mixture was bubbled through the water and into the chamber CF_3CHO, $CF_3CH(OH)_2$, and H_2O were observed in concentrations of 7.8 mTorr, 1.7 mTorr, and 2.8 Torr, respectively. Presumably the balance (79%) of the original remained as CF_3CHO and/or $CF_3CH(OH)_2$ in solution in the bubbler. We conclude that (i) gas-phase CF_3CHO reacts rapidly with liquid water, (ii) under the present experimental conditions the majority of the products are retained in liquid water, and (iii) variation of pH over the range 2−7 does not change the first two conclusions.

The second set of experiments was conducted to test for reaction of gas-phase CF_3CHO with gas-phase H_2O. In a control experiment, it was established that the loss of CF_3CHO in a dry chamber (dried by evacuating and flushing with dry air) was less than 2% over a period of 23 h. Following the control experiment two experiments were conducted in which mixtures of 16.2 mTorr of CF_3CHO and 5 Torr of water in 700 Torr of air were allowed to stand in the dark. In the first experiment the mixture was left for 13 h; in the second experiment the mixture was left for 22 h. As seen in Figure 7, in both experiments a significant decay of CF_3CHO, and formation of $CF_3CH(OH)_2$, was observed. The fact that different rates of reaction were observed in the two experiments suggests that the reaction was heterogeneous in nature. Interestingly, the yield of $CF_3CH(OH)_2$ (see insert in Figure 7) in both experiments was similar and was 0.73 ± 0.09. The missing carbon is probably attributable to CF_3CHO, $CF_3CH(OH)_2$, or both, dissolved in a surface layer of water on the chamber walls. From the CF_3CHO loss in the experiment lasting 23 h we derive an upper limit to the homogeneous reaction of $k(CF_3C(O)H+H_2O) < 2 \times 10^{-23}$ cm^3 molecule^{-1} s^{-1}.

Finally, in the third set of experiments, mixtures containing 5.6 mTorr of $CF_3CH(OH)_2$ in 700 Torr of air were admitted into an initially dry chamber and left to stand in the dark. The amount of water unavoidably introduced into the chamber with the hydrate was 100 mTorr. $CF_3CH(OH)_2$ decayed slowly (56% loss in 22 h) and was replaced by CF_3CHO. Given the long time scale, we cannot exclude the possibility that the dehydration occurs on the surface of the chamber. In fact, given the evidence for a heterogeneous component of the reverse hydration reaction, it seems likely that dehydration proceeds, at least in part, via a heterogeneous mechanism.

4. Implications for Atmospheric Chemistry

A large body of self-consistent data is presented that improves our understanding of the atmospheric chemistry of $C_xF_{2x+1}CH(OH)_2$. $CF_3CH(OH_2)$ reacts with Cl atoms and OH radicals with rate constants of $(5.82 \pm 0.92) \times 10^{-13}$ and $(1.22 \pm 0.26) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. The reactivity of $C_xF_{2x+1}CH(OH)_2$ ($x = 3, 4$) toward Cl atoms is indistinguishable from that of $CF_3CH(OH_2)$. On progressing through the series of perfluorinated aldehyde hydrates, $C_xF_{2x+1}CH(OH)_2$, the greatest change in chemical environment of the C−H bond occurs on moving from $CF_3CH(OH)_2$ to $C_2F_5CH(OH)_2$. Given our finding that the reactivity of Cl atoms toward $C_3F_7CH(OH)_2$ and $C_4F_9CH(OH)_2$ is indistinguishable from that with $CF_3CH(OH)_2$, it seems reasonable to generalize our results to all members of the $C_xF_{2x+1}CH(OH)_2$ series. Taking the average of our results, we arrive at $k(Cl+C_xF_{2x+1}CH(OH)_2) = (5.92 \pm 0.88) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k(OH+C_xF_{2x+1}CH(OH)_2) = (1.22 \pm 0.26) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Quoted uncertainties were chosen to encompass the extremes of the individual determinations.

The value of $k(OH+C_xF_{2x+1}CH(OH)_2)$ can be used to provide an estimate of the atmospheric lifetime of $C_xF_{2x+1}CH(OH)_2$ with respect to reaction with OH radicals. Using the rate constant measured at 296 K together with $[OH] = 1.0 \times 10^6$ molecule cm^{-3} [26] leads to an estimate of the atmospheric lifetime of $C_xF_{2x+1}CH(OH)_2$ of approximately 90 days. The approximate nature of this atmospheric lifetime estimate should be stressed. The average daily concentration of OH radicals in the atmosphere varies significantly with both location and season, and the local lifetime with respect to reaction with OH will also vary significantly.[27]

Hydrolysis of CF_3CHO and dehydration of $CF_3CH(OH)_2$ were investigated in the smog chamber, and for these processes we can make the following conclusions: (i) gas-phase CF_3CHO is lost rapidly (79−82% loss in approximately 2 s residence time in bubbler) on contact with liquid water; (ii) at least some of the reaction produces hydrate (the NMR study described in section 3.5 indicates that hydration is the sole fate of C_2F_5CHO on contact with liquid water); (iii) homogeneous gas-phase reaction of CF_3CHO with H_2O occurs slowly, if at all; (iv) in a relatively dry environment ($[H_2O] = 0.1$ Torr) the gas-phase hydrate $CF_3CH(OH)_2$ loses water slowly (probably via heterogeneous decomposition) to give CF_3CHO in a yield indistinguishable from unity.

At this point it is germane to note the existence of several other removal mechanisms for $C_xF_{2x+1}CH(OH)_2$. In addition to reaction with OH radicals, organic compounds are removed from the atmosphere via photolysis, wet deposition, dry deposition, and reaction with NO_3 radicals, Cl atoms, and O_3. For saturated compounds such as $C_xF_{2x+1}CH(OH)_2$, reaction with NO_3 radicals and O_3 are typically too slow to be of importance. The average concentration of Cl atoms in the troposphere is several orders of magnitude less than that of OH radicals.[28] In the present study we observe that Cl atoms are 5 times more reactive than OH radicals toward $C_xF_{2x+1}CH(OH)_2$; hence, loss via reaction with Cl atoms will not be an important atmospheric loss mechanism for $C_xF_{2x+1}CH(OH)_2$. Alcohols do not absorb at UV wavelengths > 200 nm,[29] and fluorination causes a blue shift in their UV spectra.[30] It is likely that gem-diols express similar properties, and thus, photolysis of $C_xF_{2x+1}CH(OH)_2$ will not be important in the troposphere.

Estimation of the significance of wet and dry deposition for $C_xF_{2x+1}CH(OH)_2$ is complicated by the lack of physicochemically relevant parameters for perfluorinated aldehyde hydrates. Given the water solubility of $C_xF_{2x+1}CH(OH)_2$, it seems likely that incorporation into rain−cloud−seawater will be a significant atmospheric removal mechanism for the short-chain hydrates. While reaction of the hydrates with OH in the aqueous phase is a potential source of PFCAs, the NMR results in the present work suggest the importance of partitioning of the hydrates back into the gas phase where their fate will be dictated by gas phase OH chemistry. This process is expected to increase in importance for the more environmentally relevant long-chain hydrates such as $C_8F_{17}CH(OH)_2$ with long hydrophobic fluorinated tails that are less soluble and will likely reside at the gas−water interface where they can evaporate into the gas phase. It is difficult to estimate the rate of wet deposition for these long-chain hydrates.

We show here that reaction of Cl atoms with $C_xF_{2x+1}CH(OH)_2$ proceeds via H-atom abstraction to give $C_xF_{2x+1}C{\bullet}(OH)_2$ radicals. The sole atmospheric fate of $C_xF_{2x+1}C{\bullet}(OH)_2$ radicals is reaction with O_2 to give the corresponding perfluorinated carboxylic acid, $C_xF_{2x+1}COOH$, and HO_2. For saturated compounds with only one type of reactive C−H bond such as $C_xF_{2x+1}CH(OH)_2$ the products of reaction with OH radicals are expected to be the same as those for reaction with Cl atoms. Hence, from the results presented in section 3.3 we conclude that OH radical initiated oxidation of $C_xF_{2x+1}CH(OH)_2$ gives the corresponding perfluorinated carboxylic acid. Atmospheric oxidation of $C_xF_{2x+1}CH(OH)_2$ hydrates could be a significant source of perfluorinated carboxylic acids in the environment. However, it is difficult to provide a quantitative assessment of the environmental relevance of this source of perfluorinated carboxylic acids given the absence of information concerning (i) the equilibrium between $C_xF_{2x+1}CHO$ and $C_xF_{2x+1}CH(OH)_2$ under environmentally relevant conditions and (ii) the rate of wet deposition of $C_xF_{2x+1}CH(OH)_2$. Further work in this area is needed.

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Supporting Information Available: Description of spectral analysis and figures showing the IR spectra of a mixture of $CF_3CH(OH)_2$, CH_4, and Cl_2 and IR spectral analysis of $CF_3CH(OH)_2$ and CH_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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